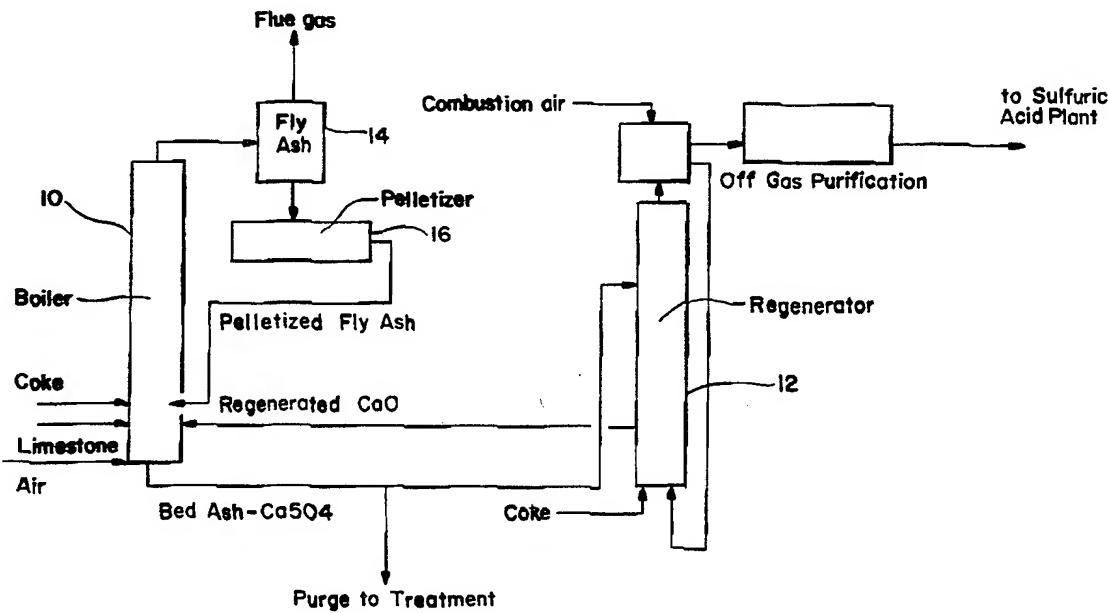




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : F23C 11/02		A1	(11) International Publication Number: WO 94/21965 (43) International Publication Date: 29 September 1994 (29.09.94)
(21) International Application Number: PCT/US94/02762		(74) Agent: JACKSON, David, A.; Klauber & Jackson, 411 Hackensack Avenue, Hackensack, NJ 07601 (US).	
(22) International Filing Date: 15 March 1994 (15.03.94)		(81) Designated States: AU, BB, BG, BR, BY, CA, CN, CZ, FI, HU, JP, KP, KR, KZ, LK, LV, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SK, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
(30) Priority Data: 08/031,537 15 March 1993 (15.03.93) US		(60) Parent Application or Grant (63) Related by Continuation US 08/031,537 (CIP) Filed on 15 March 1993 (15.03.93)	
(71) Applicant (for all designated States except US): COMMUNITY ENERGY ALTERNATIVES INCORPORATED [US/US]; 1200 East Ridgewood Avenue, Ridgewood, NJ 07450-3939 (US).		Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	
(72) Inventors; and (75) Inventors/Applicants (for US only): NISLICK, Arthur, S. [US/US]; 317 Rodney Road, Wycoff, NJ 07004 (US). BAUER, Arthur, M. [US/US]; 106 Prospect Terrace, Tenafly, NJ 07670 (US). WEISS, Alfred, J. [US/US]; 7 Willow Lane, Tenafly, NJ 07670 (US).			

(54) Title: RECYCLING PROCESSES USING FLY ASH



(57) Abstract

CaO is regenerated and recycled from a bed ash stream of a fluidized bed combustion boiler (10), in particular a petroleum coke fired fluidized bed combustion boiler, in which the particle size of fly ash, which contains CaO and CaCO₃, is increased by agglomeration or pelletization, and then returned to the boiler. Bed ash, containing CaSO₄, is passed to a regeneration zone (12), heated to a temperature of from about 1,000 °C to about 1,150 °C, to provide a solid phase containing CaO and a gas phase containing SO₂. The solid CaO is then recycled to the fluidized bed combustion boiler. Such recycling and regeneration schemes enable a large number of recycles of CaO and CaCO₃ to be carried out without loss of sulfur absorption capacity of the CaO and CaCO₃.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

RECYCLING PROCESSES USING FLY ASH

TECHNICAL FIELD OF THE INVENTION

The present invention relates generally to the removal of sulfur from the waste stream from a petroleum product fired fluidized bed boiler, and more particularly, to the recirculation of fly ash from a petroleum coke- or coal-fired fluidized bed boiler to serve as a sulfur sorbent, and the concomitant recovery of the metallic impurities present in coke.

BACKGROUND OF THE INVENTION

- 10 Power and/or steam generation plants, fired by fossil fuels such as coal or petroleum coke, often employ fluidized beds as the means for combusting the fossil fuel and as the means for converting the energy from the fossil fuel into electric power. Fossil fuels such as coal and petroleum coke contain sulfur which during combustion, is converted to sulfur dioxide, or SO₂. To limit sulfur
- 15 emissions to acceptable levels as required by environmental regulatory agencies, limestone and/or dolomite is injected into the combustion zone of the boiler. CaCO₃, the major constituent of limestone and dolomite, is converted to CaO and CO₂, when exposed to the combustion zone temperature of the boiler. CaO reacts with SO₂ to form calcium sulfate or gypsum, or CaSO₄. To insure that sulfur
- 20 emission is reduced to the required levels, it is typical to use an excess amount of CaO so that the resultant ash will contain CaSO₄ and unreacted CaO.

- In circulating fluidized bed combustion boilers, two ash streams, known as bed ash and fly ash, are generated. Montagna, et al., The Proceedings of the Fifth International Conference on Fluidized Bed Combustion (Washington, D.C., December 13-14, 1977), pgs. 776-794, disclose the regeneration of CaO from CaSO₄ from the ash formed in a coal-fired fluidized bed combustion process development unit. The development unit only generates one type of ash as its operation does not represent the operation of a typical fluidized bed combustion boiler that generates bed ash and fly ash. Montagna, et al. also disclose a flow

sheet that shows a concept of a full scale fluidized bed combustion boiler using coal as the fuel. In this concept, it is indicated that the fly ash is disposed of without recycling it to the fluidized bed combustion boiler. In the same article, it also is shown that after a number of regeneration cycles the recovered CaO loses 5 its sulfur sorbent capacity. In the regeneration process described in the article, the ash containing CaSO_4 is heated to about 1100°C . The heat is provided by the combustion of a fuel such as coal or natural gas. This combination yields a reducing gas containing carbon monoxide (CO) which reacts with CaSO_4 to form CaO , CO_2 , SO_2 and H_2O . In another process, CaSO_4 is reacted with a reducing 10 gas at about 870°C to form CaO . The CaO is then reacted with steam and carbon dioxide at about 560°C to produce CaCO_3 and H_2S .

Petroleum coke, which is obtained from the refining of crude oil, has properties similar to that of coal except that its ash content and moisture content, in general, are much lower, which results in a higher heat content. Petroleum coke, however, 15 has a sulfur content that may range from about 1% to about 7%. Typically, the amount of limestone (CaCO_3) injected into the combustion zone of a petroleum coke fired fluidized bed combustion boiler is considerably in excess of the stoichiometric quantity required to convert all of the SO_2 to CaSO_4 , so that the ash generated during combustion contains CaSO_4 , unreacted CaO , undecomposed 20 CaCO_3 , and small quantities of vanadium, nickel, and other elements introduced into the combustor with the petroleum coke and limestone.

In general, both the bed ash and the fly ash are removed from the petroleum coke fired fluidized bed combustion boiler, and are disposed of either as a landfill or as a source for making cement. The disposal of the ash streams as landfill will 25 become increasingly limited as those ash streams are or will be classified as hazardous wastes due to the presence of vanadium and nickel in these streams, and to this extent, alternative processes are being actively investigated. It is in this context that the present applicants first proposed the recycling and regeneration of the ash component of circulating fluidized bed combustion to serve as a sorbent for

sulfur and to assist in the recovery of the metal by-products of this combustion. Prior to the present invention, the use of ash in either capacity was unknown.

The role of ash in desulfurization or other recovery processes is further considered below. More particularly, U.S. Patent No. 4,197,285 to Yang et al. discloses the
5 removal of sulfur oxides by sorption with calcium oxide or lime, which is regenerated by heat treatment in contact with a source of carbonaceous material, after which it is recycled to the fluidized bed combustor to abstract further sulfur oxides. Yang et al. is reflective of the prior art, in that such processes, even with regeneration as disclosed, require a substantial input of exogenous lime for their
10 continued operation.

Some of the difficulties that attend the continuous desulfurization using reducing gas atmosphere and the like are reflected in U.S. Patent No. 4,686,090 to Howell et al. The patentees generally discuss the use of calcium oxide and its treatment in a regenerating system under reducing conditions and at temperatures of upwards of
15 1,000°F. The patentees comment that the efficiency of this process is low, and attendant problems exist in the disposal of the spent sorbent owing to its toxicity to air and ground water.

U.S. Patent No. 4,710,365 to Gebhard et al., while directed to a dry process for desulfurization and thereby distinguishable from that of the present invention,
20 discuss in general the value of recirculating a sorbent which may include fly ash. Gebhard et al., however, propose to mill or grind their sorbent before return to the flue gas (column 3, lines 6-10).

U.S. Patent No. 4,782,772 to Chughtai et al. relates to the purification of the flue gas emitted by a grate firing steam generator. Chughtai et al. disclose the use of
25 flue gas and particularly suggest its hydration, in combination with an additive such as calcium hydroxide or calcium carbonate and subsequent return to the combustion unit. It is not clear from Chughtai et al. as to what functions as the

sorbent, and clearly, there is no disclosure of the agglomeration or other increase in particle size of the sorbent to achieve the benefits of the present invention.

U.S. Patent No. 4,867,955 to Johnson relates to desulfurization of combustion gases by decalcination of a compound amenable to such treatment within the 5 combustion chamber, and its processing with fly ash and subsequent return to the combustion chamber to serve as a sorbent. The primary aspect of Johnson appears to be in the use of the calcinable material and in its full calcination to effect desulfurization. There is no disclosure of the use of fly ash or, more importantly, its regeneration and particle size accretion to limit the requirements of limestone 10 and other exogenous materials.

U.S. Patent No. 4,600,568 to Yoon et al. discloses the desulfurization of flue gas by mixing with calcium hydroxide, and subsequently spraying the suspension with an aqueous solution of either a deliquescent compound or strongly ionizing inorganic salt. The only disclosure with respect to Yoon that may have any 15 bearing on the present invention is the regeneration and recycling of the sorbent after its separation from flue gas. Likewise, U.S. Patent No. 4,604,269 to Yoon discloses the desulfurization of flue gas by treatment with a finely divided sorbent such as calcium or magnesium hydroxide and the activation of the sorbent by its slaking with water along with the add-in of makeup sorbent such as quick lime, 20 for regeneration during the operation of the process. There is no disclosure of the use of flue gas in the capacity as presently, as a sorbent, and in a process where it is increased in particle size and constantly recycled through the combustion unit.

U.S. Patent No. 4,609,536 to Yoon et al. is cumulative with the earlier disclosure to this inventor, as limestone is shown being calcined and utilized as a sorbent.

25 Japanese Application No. 87-157609/23 to Onoda Cement KK discloses the preparation of a desulfurization agent for use in fluidized bed combustion heating, where limestone or dolomite, cement and water are mixed and recirculated.

Reference is made to fly ash cement, and to the use of fly ash or other like material as a seed material for the preparation of the desulfurizing agent or sorbent. There is no disclosure of the use of fly ash in the fashion contemplated herein.

- 5 Japanese Application No. 89-360962/49 to Babcock-Hitachi KK similarly relates to a dry type flue gas desulfurization which uses fly ash containing high lime, where fly ash having this high lime is collected from the flue gas and thereafter where water is added to the fly ash and the fly ash thereafter mixed and hydrated. The particular method employed in this disclosure is distinguishable from the fluidized
- 10 bed environment of the present invention, and there is moreover no disclosure of the specific recycling and agglomeration of fly ash in accordance with the present invention.

During the prosecution of Applicants' parent application, certain patent references were cited. Specifically, U.S. Patent No. 4,256,703 to Dixit et al. was cited for its disclosure of the use of fly ash for the recovery of dust particles in utility furnace systems with electrostatic precipitators. Immediately, the environment of the present invention is clearly distinguishable from that of Dixit et al., inasmuch as the operation of fluidized bed boilers of the type contemplated herein is in sharp distinction to the electrostatic precipitator of utility furnaces. More to the point, there is no disclosure in Dixit et al. of anything more than the removable fly ash, and clearly no appreciation of the role that fly ash plays in the present invention, where it is utilized as a sorbent, and is recirculated and agglomerated to this purpose. The essence of the Dixit et al. disclosure is the inclusion of an additive to combine with fly ash particles to increase their size to render them better responsive to electrostatic precipitation and other forms of mechanical separation. There is no disclosure therefore in Dixit et al. of the nature of the present invention, i.e., the circulation and recycling in a fluidized bed boiler of fly ash as a sulfur sorbent.

U.S. Patent No. 5,044,286 to Breen et al. directs itself to the recycling of fly ash in a wet bottom furnace. In like fashion to Dixit et al., Breen et al. are concerned with a different form of combustion unit and, moreover, have as their purpose the recycling of fly ash merely for the purpose of melting same so as to retrieve it as liquid slag. There is no appreciation of the use of fly ash as a sorbent for sulfur or other similar effluents and that the increase in particle size is for the purpose of achieving greater activity and lifespan as a sorbent and concomitantly reducing the need for the inclusion and addition of exogenous sorbent materials. The Breen et al. disclosure is accordingly directed to the exclusive retrieval and disposal of fly ash and not to its use as a sorbing agent.

Lastly, U.S. Patent No. 3,683,626 to Merrill is totally unrelated to the present invention, as it seeks to purify the exhaust from internal combustion engines. This effluent and its source are in sharp distinction to the atmosphere and operation of a fluidized bed combustion boiler. Merrill proposes to condense certain of the particulate effluent by use of water vapor and to reintroduce the condensate into the engine for better and more efficient combustion. It is not the intention of Merrill to create and perpetuate the successful use of fly ash or like effluent as a sorbent. Merrill is significantly far removed from the present invention, and any teachings however tangential cannot be applicable hereagainst.

20 A need therefore exists for the development of a more efficient, economical and environmentally acceptable method for the recovery, and reuse and disposal of the by-products of power plant combustion.

SUMMARY OF THE INVENTION

In accordance with an aspect of the present invention, there is provided a process 25 for the recovery of the by-products of the operation of a circulating fluidized bed combustion boiler, including sulfur dioxide and metals such as vanadium and nickel. The process comprises removing fly ash containing CaO and CaCO₃ from

the circulating fluidized bed combustion boiler, increasing the particle size of the fly ash, and then returning the increased particulate ash to the circulating fluidized bed combustion boiler to serve as a sorbent.

In one embodiment, the circulating fluidized bed combustion boiler is a petroleum coke fired circulating fluidized bed combustion boiler. In another embodiment, the circulating fluidized bed combustion boiler is a coal fired circulating fluidized bed combustion boiler.

As mentioned, the particle size of the fly ash may be increased by agglomerating or pelletizing the fly ash. Specifically, the particle size of the fly ash may be increased by admixing the fly ash with a binder component, followed by 10 agglomeration or pelletization. A particularly suitable binder component is water.

Accordingly, it is a principal object of the present invention to provide a method for the efficient and economical desulfurization of the effluent of certain petroleum-product fired fluidized bed boilers and the like, by the recycling of fly 15 ash and regeneration of bed ash as a sulfur sorbent.

It is a further object of the present invention to provide a method as aforesaid that serves as a method for the recovery of sulfur dioxide.

It is a further object of the present invention to reduce the amount of fresh limestone required for controlling sulfur emissions, and to reduce the amount of 20 ash streams that must be disposed of from the boiler.

Other objects and advantages will become apparent to those skilled in the art from a consideration of the ensuing detailed description which proceeds with reference to the following illustrative drawing.

BRIEF DESCRIPTION OF THE DRAWING

FIGURE 1 comprises a flow diagram illustrating a scheme for the recirculation and regeneration of fly ash as a sorbent in a petroleum coke fired fluidized boiler, in accordance with an embodiment of the present invention.

- 5 FIGURE 2 is a graph demonstrating the advantage in the use of the sorbent of the present invention over the use of limestone.

DETAILED DESCRIPTION

Accordingly, in a first aspect of the present invention, a method is disclosed for the recovery of sulfur dioxide from the effluent of a circulating fluidized bed

- 10 (CFB) combustion unit such as a boiler, by the recycling of the ash component to regenerate same to serve as a sorbent.

More particularly, the fly ash component is subjected to particle size accretion such as by agglomeration or pelletization, and is then reintroduced to the combustion environment. The bed ash component is forwarded to a regeneration

- 15 unit where it is treated to separate the ash into a solid component containing CaO and a gaseous component containing SO₂.

As discussed above, the method of the present invention in its primary aspect comprises the regeneration and recycling of fly ash and bed ash to serve as a sorbent for sulfur, and in a further embodiment, to participate in the recovery of

- 20 metals such as vanadium and nickel, that accumulate in the combustion process in both coal and petroleum coke-fired fluidized bed boilers. The present method is further advantageous in that its reliance on the byproducts of combustion for sorption and recovery significantly reduces and, in some instances, may eliminate the need for the consumption of exogenous sorbent material such as limestone.

The environmental advantages conferred by this process are therefore made apparent.

A further surprising aspect of the present invention is the improvement in the performance of the pellets as sorbents. As discussed in greater detail later on 5 herein, the greater size of the present fly ash particles would lead the artisan to expect that such a particle would exhibit reduced effectiveness as a sorbent, owing to experience with limestone. While not wishing to be bound to a particular theory of operation, it is proposed that the particles of the present invention are porous and thereby present an enhanced surface area which contributes to their 10 improved activity. The structure and activity of the fly ash particles of the present invention is submitted to be a significant characterizing feature thereof.

Referring now to Figure 1, a general scheme is shown wherein a fluidized bed boiler represented schematically at 10, is charged with a combustible material such as coke, and in traditional fashion, also is charged with limestone and air. As 15 mentioned earlier, the limestone contributes to the sorption of the sulfur that represents one of the byproducts of combustion. In the instance where petroleum coke is combusted, the low ash content and high combustible and high sulfur content, while contributing to its value as a fuel, is a detractor when the recovery of combustion byproducts is attempted. For this reason, and as shown 20 schematically in Figure 1, limestone is charged to serve as a sorbent for SO₂.

While the discussion is proceeding and illustrates the use of petroleum coke as the fuel, it is to be understood that other petroleum-based fuels or coal, may likewise be used. As explained earlier, fluidized bed combustion units carry with them certain specific characteristics, among them the generation of two forms of ash, 25 namely fly ash and bed ash. The object of the present invention is to achieve the recycling, recirculation and utility of each of these fractions to assist in pollution abatement and elemental recovery.

- If both fractions exit the boiler, the upper fly ash fraction is first directed to a region as indicated at 14, where flue gas may be drawn off, and the remainder of the fines may then be passed through a cyclone for further separation, and then may be directed to a baghouse and from there to the pelletizer labeled 16. The 5 exact nature of particle size increase may vary, as both pelletization and agglomeration are contemplated. For example, the fly ash may be mixed with water in two types of mixers and, for example, charged to a pin mixer to form the ultimate pelletized material. Naturally, other forms of agglomeration are contemplated, and the invention is not limited to a specific procedure or means.
- 10 The method of the present invention comprises in one of its aspects, the achievement of particle size increase by the use of a material identified herein as a binder. For purposes of the present invention, and in accordance with a preferred embodiment thereof, the binder may comprise a fine spray of water which is used for the purpose of achieving a surface wetting of the particles to facilitate their 15 accretion and agglomeration. Naturally, the invention is not limited to the use of water in this capacity.

After the increased size particles have been formed in the pelletizer 16, they are charged back into the fluidized bed boiler 10 for use as a sorbent. It is also noteworthy at this juncture that the bed ash that comprises the calcium sulfate 20 (CaSO_4) at the bottom of the fluidized bed is likewise circulated to a regenerator unit 12 where heat treatment in accordance with the present process is conducted to remove sulfur dioxide (SO_2). As illustrated herein in a particular embodiment, the material may be treated in a reducing atmosphere and at temperatures ranging from about 1000°C to about 1150°C, with a temperature range of from 1050°C to 25 about 1150°C being preferred. Thus, the regenerated calcium oxide-bed ash particles may be returned to the fluidized bed boiler in much the same fashion as the pelletized fly ash, to participate in similar fashion, as a sorbent, as well as in the combustion process.

- While the foregoing explanation and illustration are strictly schematic and general in nature, they outline certain of the salient aspects of the invention, namely the ability to draw upon endogenous material from the combustion process to achieve pollution abatement without the need for substantial input of exogenous sorbent
- 5 material. The advantage of this method is clear, in that an efficient utilization of materials is achieved together with reduced environmental impact, from the standpoint of the reduction in the toxicity of the emissions and the quantity of solid effluent, and the recovery of certain elemental materials such as the metals contained within the ash component.
- 10 In this latter connection, the continued recirculation of the ash component in its capacity as sorbent has been found to ultimately develop sufficient metal content so as to facilitate the processing of the material by other means known in the art, to recover the metals therefrom as discussed herein. The specific metals that are capable of recovery in accordance with the present invention are vanadium and
- 15 nickel, and the invention in this connection is predicated upon the continuous performance of the within method until the ash component contains the threshold percentage of metal. Periodic monitoring of the composition of the ash component is conducted to identify the stage at which the ash component contains the requisite minimum amount of metal to merit separation of the latter for recovery.
- 20 A typical sieve analysis of the fly ash from the circulating fluidized bed combustion boiler is as follows:
- | | <u>Screen Mesh</u> | <u>% Retained</u> |
|----|--------------------|-------------------|
| | 230 | 18.3 |
| | 325 | 29.2 |
| 25 | 400 | 44.7 |
| | >400 | 7.9 |

In one embodiment, the admixture of the fly ash and water is done consecutively in two separate types of equipment. The fly ash first is mixed with water in a

conditioner, and then in a pin mixer. In one specific embodiment, 600 pounds of fly ash with a sieve analysis similar to that hereinabove described is mixed with 180 pounds of water in a conditioner at room temperature and atmospheric pressure and rotated for a few minutes at 300 rpm. The mixture is then charged 5 to a pin mixer, in which the mixture may be processed at 750 rpm for a few minutes at room temperature and atmospheric pressure. The result of the above-mentioned mixing steps is the production of pellets having a size distribution with the following sieve analysis:

	<u>Screen Mesh</u>	<u>% Retained</u>
10	6	1.0
	8	16.1
	10	13.6
	12	11.6
	16	32.9
15	20	13.4
	30	5.5
	45	3.6
	120	1.1
	200	0.6
20	>200	0.4

As discussed above, it has been found that, by removing the fly ash from the combustion boiler and increasing the particle size, the fly ash may be successfully reused as a sulfur sorbent. The recycled CaO and CaCO₃ will combine with the SO₂ formed in the combustion zone in the boiler, thereby decreasing the amount of 25 fresh limestone required for controlling sulfur emissions while decreasing the amount of ash to be disposed of as landfill.

In accordance with another aspect of the present invention, there is provided a process for the regeneration of CaO from bed ash containing CaSO₄ in a petroleum coke fired circulating fluidized bed combustion boiler. The process comprises

removing bed ash containing CaSO_4 from the circulating fluidized bed combustion boiler, and passing the bed ash to a regeneration zone. The bed ash is heated under fluidized bed conditions in the regeneration zone to a temperature of from about $1,000^{\circ}\text{C}$ to about $1,150^{\circ}\text{C}$, thereby forming a solid phase which includes

5 CaO and gas phase which includes SO_2 . The solid phase is then returned to the petroleum coke fired fluidized bed combustion boiler.

Preferably, the bed ash is heated in the regeneration zone to a temperature of from about $1,050^{\circ}\text{C}$ to about $1,150^{\circ}\text{C}$, and, in a preferred embodiment, the heat supplied to the regeneration zone may be generated through the combustion of

10 coke or natural gas under reducing conditions, whereby the resulting gas stream composed of CO , CO_2 , H_2 , and N_2 causes the CaSO_4 contained in the bed ash to decompose into a solid phase containing CaO and a gas phase containing SO_2 .

The recycle and/or regeneration of CaO and/or CaCO_3 from bed ash or fly ash, in addition to the advantages hereinabove described, enables one to concentrate and

15 recover metals from the ash streams of the boiler, as opposed to disposing of these metals in a landfill. Accordingly, a further aspect of the present invention relates to the recovery of metals such as vanadium and nickel by the recycling and regeneration of the ash component of the combustion of a circulating fluidized bed boiler or the like, performed on a continuous basis with the monitoring of the

20 metal content of the sorbent to determine when a threshold metal content is reached, whereupon the sorbent is subjected to chemical treatment to recover the metal compounds.

Specifically, after several cycles of regeneration, the metal content of the bed ash will increase in direct proportion to the number of regeneration cycles. When the

25 metal content reaches the desired threshold value, a constant purge stream will be discharged from the bed ash stream that is recycled to the regeneration step. This purge stream, consisting of CaO , CaSO_4 , and compounds of vanadium and nickel, will be treated in a series of chemical operations that will separate the vanadium

and the nickel from this waste stream, resulting in a gypsum product that is free of toxic compounds. The chemical operations begin by mixing the waste stream with water and sulfuric acid in a leaching vessel where the metals are dissolved in sulfuric acid. This step is followed by a liquid-solid separation step where the
5 calcium sulfate is removed from the liquid and becomes available as a non-hazardous by-product for the manufacture of cement or wallboard, or can be recycled to the regenerator to be reused as a sulfur sorbent in the boiler.

The liquid containing the metals is mixed with sodium hydroxide (NaOH) causing the vanadium to precipitate. This step is followed by a second liquid solid
10 separation and the removal of the vanadium compound for sale or further treatment.

The liquid from this second liquid-solid separation is mixed with sodium hydroxide (NaOH) and sodium carbonate (Na₂CO₃) causing the precipitation of nickel. This step is followed by a third liquid separation step and the removal of nickel
15 compounds for sale or for further treatment. The residual liquid is recycled for mixing with the incoming purge stream removed from the bed ash and flowing to regeneration.

The invention will now be described with respect to the following examples; however, the scope of the present invention is not intended to be limited thereby.

20

EXAMPLE 1

Petroleum coke, at the rate of 14460 lb/hr, is charged to a circulating fluidized bed boiler. The coke has a sulfur content of 2.78 wt%, and has 565 ppm of vanadium and 419 ppm of nickel. The boiler is operated with a CaO/S molar ratio of 2.69 and requiring a CaO feed of 1892 lb/hr. Without the process of the
25 invention this operation requires a constant fresh limestone feed of 3841 lb/hr. The limestone contains 49.26% of CaO or 88% of CaCO₃. The boiler produces

1651 lb/hr or bed ash and 1797 lb/hr of fly ash. In a typical operation, the bed ash will contain 60% of CaSO₄, 33% of CaO and smaller percentages of Al₂O₃, SiO₂, Fe₂O₃, Ni and V. The metals are introduced with the petroleum coke while the alumina and silica are part of the limestone.

- 5 The bed ash is transported to the regenerator where it is contacted with a reducing gas composed of CO, H₂, CO₂, and N₂. The reducing gas is formed from the combustion of petroleum coke and air. The heat of combustion of petroleum coke increases the temperature in the regenerator to a range of 1000°C to 1150°C.

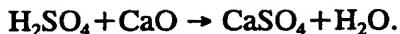
The regenerator is operated within a fluidized bed mode formed from the bed ash.

- 10 During the operation CO reacts with CaSO₄ to form a CaO, SO₂ and CO₂. The gas stream leaving at the top of the regenerator contains from 6.5% to 11% of SO₂ and is available as a raw material for the production of sulfuric acid.

The solid material is composed of CaO and small percentages of the inorganic compounds present in the bed ash. This solid stream is recycled to the circulating

- 15 fluidized bed combustion boiler and the CaO is charged into the combustion zone to repeat the process of sulfur sorption. A large percentage of the CaO is converted to CaSO₄. After several cycles of regeneration and sulfation the concentration of the metals in the ash increases. In this example, after 15 cycles of regeneration the vanadium and nickel content in the bed ash reaches a value of
- 20 2.97 and 1.8%, respectively. At this time a purge stream is removed from the bed ash as it is transported to the regenerator. The purge stream contains 167 lb/hr of CaO which is replaced by fresh limestone charged to the combustion zone of the circulating fluidized bed combustion boiler. As the limestone contains 49% of CaO, the total charge of make up limestone is 397 lb/hr.

- 25 The purge stream is discharged continuously from the system at a rate such that 8.2 lb/hr of vanadium and 6.1 lb/hr of nickel are removed from the system. The purge stream is first treated with sulfuric acid according to the equation:



In order to insure that all of the CaO is converted into CaSO₄, an excess of sulfuric acid is used. After completing the acidulation of CaO, the formed CaSO₄ is removed and returned to the regenerator or disposed of as a gypsum by-product.

- 5 The liquid from the sulfation step is reacted with sodium hydroxide, thereby causing the precipitation of vanadium compound, which is removed from the system and is available for further metallurgical refinement.

Most of the remaining liquid stream is recycled to the leaching step and small purge stream is discharged from the purge stream treatment operation.

- 10 The 1797 lb/hr of fly ash, containing about 34% of CaSO₄, 21% of CaO and 30% of CaCO₃ is removed from the flue gas of the boiler after passing through a baghouse, where essentially all of the solid matter is collected from the flue gas. The collected fly ash is mixed with 540 lb/hr of water in a conditioner where it is rotated at 300 rpm for several minutes and then charged into a pin mixer where
- 15 the mixture is processed at 740 rpm for several minutes. During this two step operation the fly ash particle size distribution is changed from a screen analysis of 230 mesh to 400 mesh to a particle size distribution with a screen analysis of 6 to 200 mesh. The larger particle size fly ash is now returned to the combustion zone of the circulating fluidized bed combustion boiler.
- 20 The increase in particle size of the fly ash in the conditioner and the pin mixer is accomplished at room temperature and atmospheric pressure.

- The combination of the regeneration of CaO from the bed ash and the recycling of the fly ash after agglomeration and an increase in the particle size distribution of the fly ash results in reducing the amount of fresh limestone that must be added
- 25 from 3841 lb/hr to 397 lb/hr.

EXAMPLE 2

The use of fly ash pellets as a sorbent supplement has the potential to significantly reduce limestone requirements. Figure 2 shows the limestone and pellet feed rates required to achieve 90% sulfur retention during Test 1 (limestone) and Test 3
5 (pellets of the invention), respectively, as well as the total sorbent feed rate required for a combination of limestone and pellets. Because of the high calcium utilization for the pellets (73% compared to 37% for the limestone), the feed rate required for 90% sulfur retention was lower for the pellets than for the limestone. The calcium-to-sulfur ratio for the limestone (Test 1) was about 2.9, compared to
10 about 1.2 for the pellets (Test 3).

Based on the results shown in Figure 2, a 20% reduction in limestone feed rate would require a pellet feed rate of approximately 0.041 pounds per pound of fuel. Current testing produced about 0.029 pounds of baghouse ash per pound of fuel, enough to produce about 0.041 pounds of fly ash pellets per pound of fuel. A
15 system with a higher ratio of fly ash to total ash would provide a higher pellet feed rate, resulting in greater limestone reduction. The data demonstrate the feasibility and advantages of the present invention over conventional sorbent materials.

20 Experience with limestone as a sorbent would indicate that the particle size of the pellets is very important, and that poor performance in terms of sulfur capture would be expected from the large pellets used for these tests. One significant difference between the pellets and limestone makes the pellets such an attractive sorbent, even when large particles are used: The pellets are made up of fly ash,
25 and therefore contain very fine calcium oxide particles (<30 microns). The chemical and physical changes that occur when the fly ash is made into pellets results in a large pellet that is very porous. Therefore, the sulfur dioxide can easily penetrate into the interior of the pellet and get good contact with the fine calcium oxide particles. Because the calcium oxide particles are very small, good

utilization of the available calcium oxide is achieved. The pellets therefore have the double advantage of being composed of very fine particles, thus getting the excellent sulfur capture attributed to fine sorbents, while at the same time being themselves relatively large, thus having a long residence time in the system.

- 5 These two advantages as compared to limestone make the pellets an excellent sorbent and explain the good performance noted during these tests.

It is to be understood, however, that the scope of the present invention is not to be limited to the specific embodiments described above. The invention may be practiced other than as particularly described and still be within the scope of the
10 accompanying claims.

WHAT IS CLAIMED IS:

- 1 1. A process for the recovery of the sulfur component from the effluent of a
2 circulating fluidized bed combustion boiler, comprising:
 - 3 A. removing fly ash from a circulating fluidized bed combustion boiler;
 - 4 B. increasing the particle size of said fly ash;
 - 5 C. returning said fly ash to said circulating fluidized bed combustion
6 boiler to serve as a sorbent for said sulfur component; and
 - 7 D. recovering the fly ash of Step C. from said boiler and separating
8 said sulfur component therefrom.
- 1 2. The process of Claim 1 wherein said circulating fluidized bed combustion
2 boiler is a petroleum coke fired circulating fluidized bed combustion boiler.
- 1 3. The process of Claim 1 wherein said circulating fluidized bed combustion
2 boiler is a coal fired circulating fluidized bed combustion boiler.
- 1 4. The process of Claim 1 wherein said increasing of the particle size of said
2 fly ash comprises admixing said fly ash with a binder component.
- 1 5. The process of Claim 4 wherein said binder component comprises water.
- 1 6. The process of Claim 1 wherein said increasing of the particle size of said
2 fly ash comprises agglomerating the particles of said fly ash.
- 1 7. A process for the regeneration of CaO from bed ash containing CaSO₄ in a
2 petroleum coke fired circulating fluidized bed combustion boiler, comprising:
 - 3 A. removing said bed ash from said fluidized bed combustion boiler;
 - 4 B. passing said bed ash to a regeneration zone;
 - 5 C. heating said bed ash under fluidized bed conditions in said
6 regeneration zone to a temperature of from about 1,000°C to about

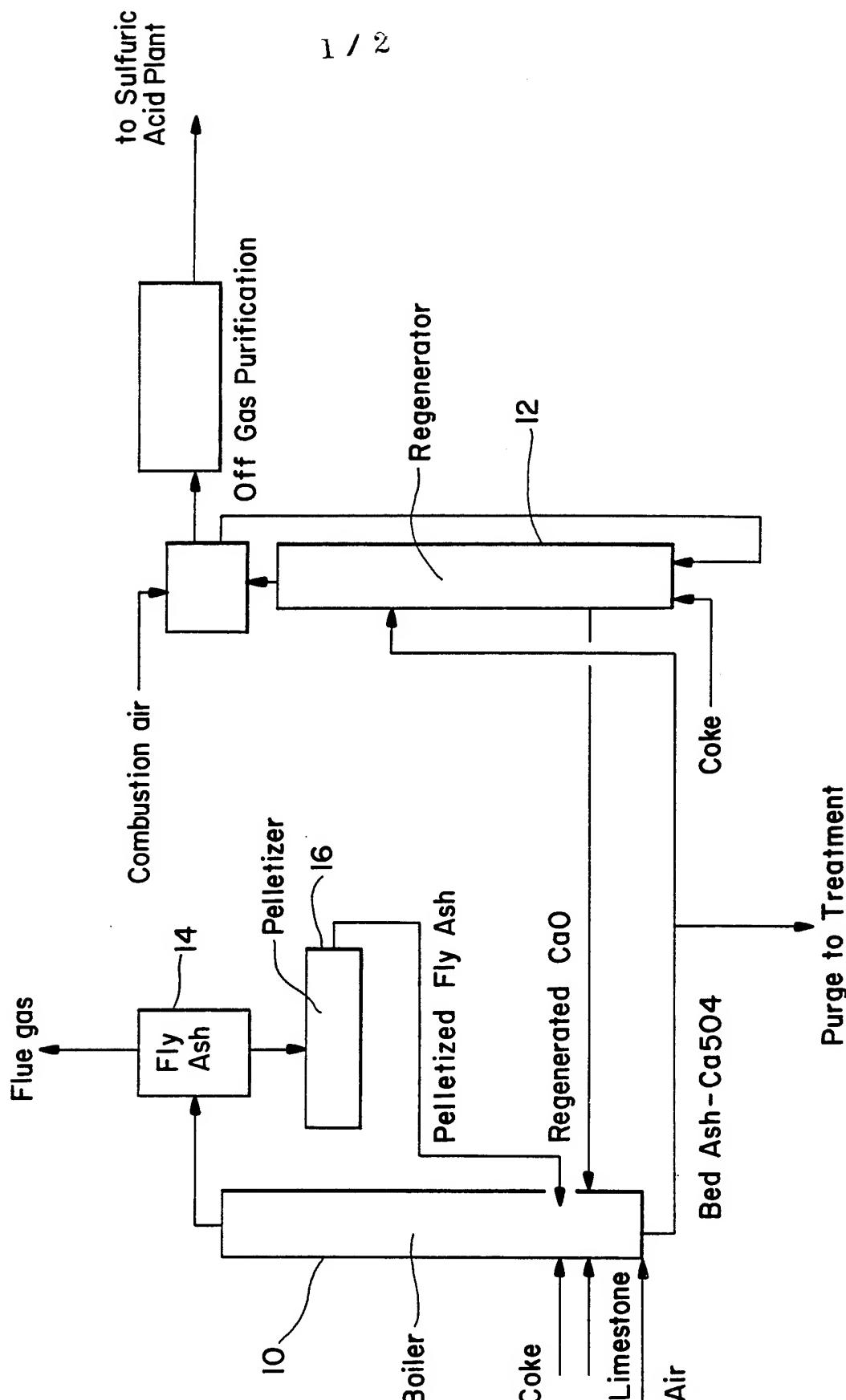
7 1,150°C, thereby forming a solid phase which includes CaO, and a gas
8 phase which includes SO₂; and
9 D. returning said solid phase to said fluidized bed combustion boiler.

1 8. A process for the recovery of metals from a fluidized bed combustion
2 boiler having bed ash as a combustion by-product, comprising:
3 A. removing said bed ash from said fluidized bed combustion boiler;
4 B. passing said bed ash to a regeneration zone;
5 C. heating said bed ash under reducing conditions in said regeneration
6 zone to form a solid phase which includes CaO, and a gas phase which
7 includes SO₂;
8 D. returning said solid phase to said fluidized bed combustion boiler;
9 E. repeating Steps A-E to increase the metal content of said bed ash;
10 and
11 F. treating the bed ash of Step E to recover said metals therefrom.

1 9. The method of Claim 7 wherein said metals are selected from the group
2 consisting of vanadium and nickel.

1 10 . The method of Claim 7 wherein said bed ash is heated to a temperature of
2 from about 1,000°C to about 1,150°C.

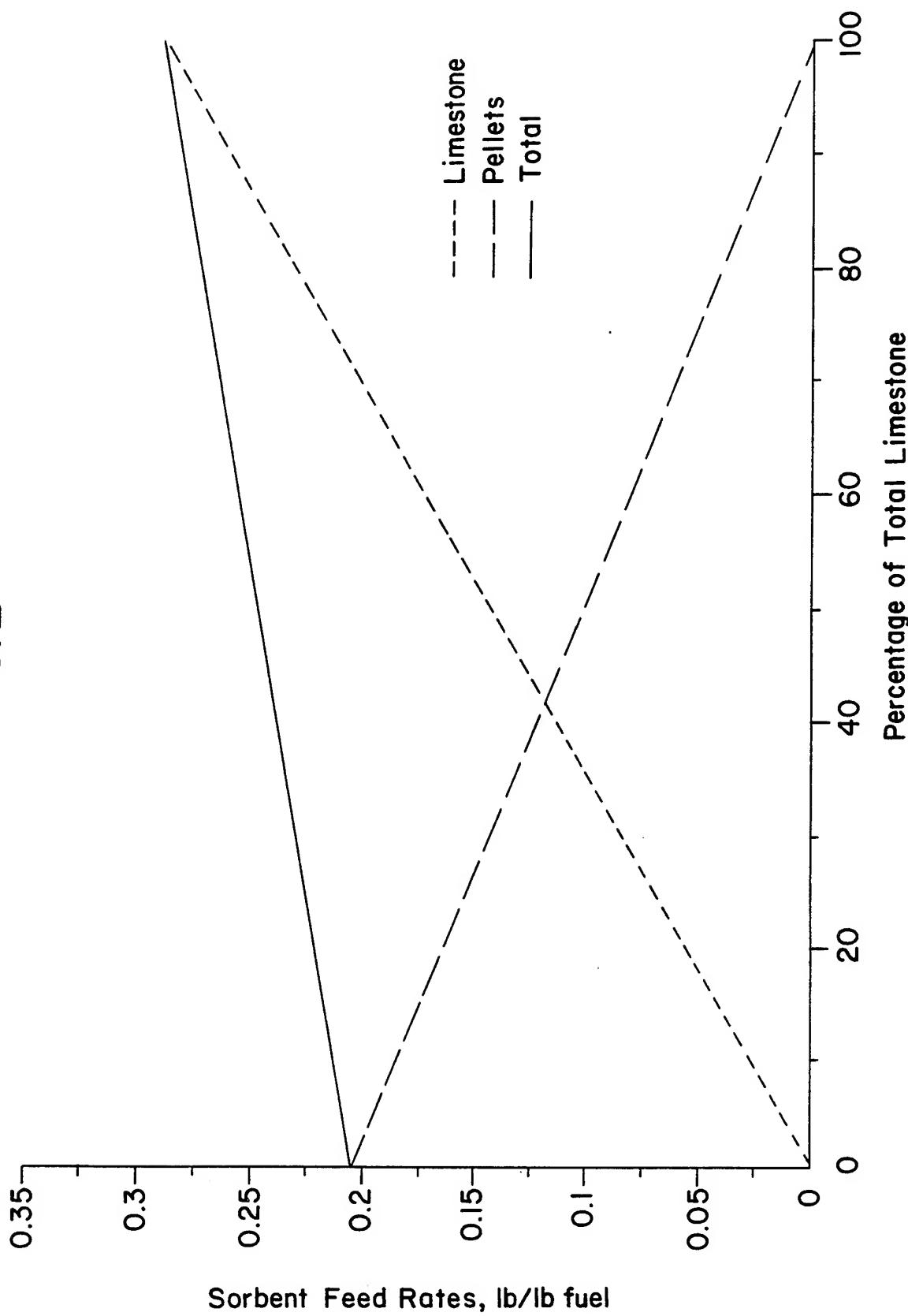
FIG. I



SUBSTITUTE SHEET (RULE 26)

2 / 2

FIG. 2



INTERNATIONAL SEARCH REPORT

Internal Application No

PCT/US 94/02762

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 F23C11/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 F23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 177 741 (STEWART) 11 December 1979 see column 1, line 44 - column 1, line 49 see column 2, line 6 - column 3, line 24 see column 3, line 61 - column 4, line 18 see figure --- 'THE PROCEEDINGS OF THE FIFTH INTERNATIONAL CONFERENCE ON FLUIDIZED BED COMBUSTION, VOLUME III' December 1977 , WASHINGTON D.C. cited in the application J.C. MONTAGNA ET AL ' Development of a process for regenerating partially sulfated limestone from fbc boilers', pages 776 - 794 see page 790 - page 792; figure 13 --- -/-/	1,3-6
A		7

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *I* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

15 July 1994

Date of mailing of the international search report

27.07.94

Name and mailing address of the ISA
 European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+ 31-70) 340-3016

Authorized officer

Phoa, Y

INTERNATIONAL SEARCH REPORT

Internal Application No

PCT/US 94/02762

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,3 807 090 (MOSS) 30 April 1974 see column 2, line 10 - column 2, line 59 see column 3, line 8 - column 3, line 13 see column 14, line 20 - column 15, line 6 see column 15, line 21 - column 15, line 34 see column 15, line 66 - column 16, line 9 see figures 11,11A,11B ----	7
A	PATENT ABSTRACTS OF JAPAN vol. 8, no. 241 (C-250) 6 November 1984 & JP,A,59 121 104 (ISHIKAWAJIMA HARIMA JUKOGYO KK) 13 July 1984 see abstract -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internal Application No

PCT/US 94/02762

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4177741	11-12-79	CA-A- 1116956 JP-C- 1180623 JP-A- 55001900 JP-B- 58015010 NL-A- 7904780	26-01-82 09-12-83 09-01-80 23-03-83 21-12-79
US-A-3807090	30-04-74	NONE	

PUB-NO: WO009421965A1
DOCUMENT-IDENTIFIER: WO 9421965 A1
TITLE: RECYCLING PROCESSES USING FLY ASH
PUBN-DATE: September 29, 1994

INVENTOR-INFORMATION:

NAME	COUNTRY
NISLICK, ARTHUR S	US
BAUER, ARTHUR M	US
WEISS, ALFRED J	US

ASSIGNEE-INFORMATION:

NAME	COUNTRY
COMMUNITY ENERGY ALTERNATIVES	US
NISLICK ARTHUR S	US
BAUER ARTHUR M	US
WEISS ALFRED J	US

APPL-NO: US09402762

APPL-DATE: March 15, 1994

PRIORITY-DATA: US03153793A (March 15, 1993)

INT-CL (IPC): F23C011/02

EUR-CL (EPC): F23C010/00 , F23C010/10 ,
F23C010/26

US-CL-CURRENT: 110/259

ABSTRACT:

CHG DATE=19990617 STATUS=0>CaO is regenerated and recycled from a bed ash stream of a fluidized bed combustion boiler (10), in particular a petroleum coke fired fluidized bed combustion boiler, in which the particle size of fly ash, which contains CaO and CaCO₃, is increased by agglomeration or pelletization, and then returned to the boiler. Bed ash, containing CaSO₄, is passed to a regeneration zone (12), heated to a temperature of from about 1,000 DEG C to about 1,150 DEG C, to provide a solid phase containing CaO and a gas phase containing SO₂. The solid CaO is then recycled to the fluidized bed combustion boiler. Such recycling and regeneration schemes enable a large number of recycles of CaO and CaCO₃ to be carried out without loss of sulfur absorption capacity of the CaO and CaCO₃.